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DEVELOPMENT OF HIGH ENERGY DENSITY
PRIMARY BATTERIES

by

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ABSTRACT

Studies of the CuF_2 -Li system for the development of high energy density primary batteries were conducted. Lithium metal stability in purified PC- LiClO_4 electrolyte was studied. Solubility of CuF_2 in PC and BL was found to increase with both water contamination level and LiClO_4 concentration. X-ray studies of dried CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ showed formation of CuOHF , $\text{CuOHF} \cdot \text{CuF}_2$ and an unknown compound. Good capacity retention was obtained with CuF_2 -Li cells with PC- LiClO_4 electrolyte after six weeks wet stand at -15°C .

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1. SUMMARY

Experimental work toward development of high energy density CuF_2 -Li primary cells was conducted.

Electrolyte Systems Studies. Lithium metal stability in purified propylene carbonate and in 1M LiClO_4 solution was studied. Stability was better in the LiClO_4 solution at ca. 150 ppm H_2O than in the solvent alone at ca. 25 ppm H_2O . Treatment with lithium powder was effective in reducing the water content in the electrolyte but did not improve lithium stability significantly.

The maximum specific conductance of NaClO_4 in propylene carbonate was found to be 6.8×10^{-3} mho/cm at 1.2 mols solute per liter of solvent. The highest conductance for LiClO_4 solutions in redistilled DMF was found to be 14.7×10^{-3} mho/cm at a concentration of 1.4 mols/liter of solvent.

The vapor pressure of 4.7M LiClO_4 solution in methyl formate was found to be 1.7 atm. abs. at 72°C .

Positive Electrode Studies. The solubility of CuF_2 in LiClO_4 solutions in propylene carbonate and butyrolactone was found to increase with the degree of water contamination of the solution. Increasing the LiClO_4 concentration increased solubility of CuF_2 to a lesser degree. The solubility was larger in butyrolactone than in propylene carbonate electrolytes.

X-ray studies of dried CuF_2 showed the main decomposition products to be CuOHF and $\text{CuOHF} \cdot \text{CuF}_2$. Decomposition of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ yielded primarily CuOHF and/or an unknown compound with a major peak intensity at 4.15 Å.

Preliminary tests have shown the unknown $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ decomposition product to have a low solubility in LiClO_4 -PC electrolyte compared to CuF_2 .

Cell Systems Studies. Tests performed with Ag_2O_2 -Li cells showed more than 70% loss of capacity after two weeks of open circuit stand at 35°C . Loss of electrolyte solvent was observed during stand, but appearance of Li electrodes was metallic at the end of open circuit stand.

CuF₂-Li cells with PC-LiClO₄ electrolyte were tested for wet shelf life capability at -15°C and +35°C. Capacity retention was good after six weeks stand at -15°C. After two weeks stand at 35°C, only two of six cells retained any capacity above 2.5V discharge potential.

Tests with CuF₂-Li cells having butyrolactone electrolyte solvent gave poor CuF₂ utilization efficiency at the 200-hour rate (20-30 percent) compared to performance of cells having propylene carbonate solvent (60-80 percent efficiency).

2. INTRODUCTION

The purpose of this program is the development of high energy density primary battery systems suitable for space flight applications. Two types of batteries, differing in energy density and discharge rate requirements, are being sought: 1) batteries capable of delivering 200 watt hours per pound at the 100-1000 hour discharge rate, and 2) batteries capable of delivering 50 watt hours per pound at the 1 hour discharge rate. For both types of batteries, the CuF_2 -Li couple is being considered. For the low-rate battery, a propylene carbonate-lithium perchlorate electrolyte system is of primary interest, while for the high rate system a methyl formate-lithium perchlorate electrolyte is being considered. These systems emerged as the most promising at the conclusion of two previous yearly contract periods (NAS 3-2775 and NAS 3-6004).

At the present time, the limited shelf life capability continues to constitute the main problem in the evolution of the Li- CuF_2 battery system. At least moderately good wet stand performance has been demonstrated for cells having PC- LiClO_4 electrolyte (6 weeks at -15°C), but at temperatures only slightly above ambient (35°C), shelf life for these cells is no better than a few days.

The objective of the major portion of the work performed during the past quarter of the contract period was the development and evaluation of methods for improving the open circuit capability of the CuF_2 -Li system.

3. DESCRIPTION OF EXPERIMENTAL WORK

3.1. ELECTROLYTE SYSTEMS STUDIES

3.1.1. Lithium Stability Tests

The detrimental effect of small amounts of water contamination on the chemical stability of lithium test strips in butyrolactone and propylene carbonate has been reported previously (NASA CR-54920). During the past quarter, stability of Li strips in propylene carbonate treated with lithium powder was studied.

Propylene carbonate was distilled at 10 mm Hg, and the water content was ascertained to be below 25 ppm. A portion of this solvent was retained, and the remainder was agitated for 40 hours with powdered lithium, filtered, and redistilled. Lithium test strips were cut to size 1 x 1/2 x 1/16 inch, and one side of each strip was abraded to expose fresh metal. The strips were then placed in test tubes containing 5 ml of solvent or 1M LiClO₄ solution under argon. The tubes were sealed and stored at 35°C, and the appearance of the lithium samples was recorded periodically.

Results of the stability tests are listed in Table I, page 5. In both lithium treated and untreated solvents, presence of 1M LiClO₄ enhanced chemical stability. In the solvent alone, lithium treatment appeared to improve stability, but this could also be a result of a lower water contamination level of this material, since additional drying probably occurs during lithium treatment. In presence of 1M LiClO₄, the stability was not significantly different with the treated and untreated materials, indicating that impurities which are not removed by distillation are not particularly reactive with metallic lithium. However, lithium treatment is used at the present time in the preparation of PC electrolytes for cell tests, since this procedure produces water contamination levels below the sensitivity of the Karl Fisher test (25 ppm) and is not particularly cumbersome to apply.

TABLE I
LITHIUM STABILITY TESTS IN
PROPYLENE CARBONATE SOLUTIONS (+35°C)

Time, Hours	Propylene Carbonate purified by distillation alone		Propylene Carbonate purified by lithium treatment and distillation	
	No solute $H_2O = (25 \pm 20) \text{ ppm}$	1N $LiClO_4$ $H_2O = 175 \text{ ppm}$	No solute $H_2O < 25 \text{ ppm}$	1N $LiClO_4$ $H_2O = 150 \text{ ppm}$
15	Cut and rough surfaces are tarnishing	No attack	Rough surface tarnishing	No attack
45	Rough surface black; cut surfaces blackening; filmed surfaces tarnishing	No attack	All surfaces tarnishing	No attack
70	No noticeable changes	No attack	No noticeable changes	No attack
160	Same	No attack	Same	No attack
210	Same	Roughened side slightly tarnished	Same	Roughened side might be tarnishing
330	Trace of gelatinous material in bottom of tube	Trace of gelatinous material in bottom of tube	Same	Same
540	All surfaces dulled except the cut ones	No noticeable changes	All surfaces dulling except the cut ones	A trace of gelatinous material in bottom of tube
1250	Gelatinous material and some powdery white material in bottom of tube; liquid phase cloudy; cut surfaces black; roughened surfaces black.	All surfaces have dulled; gelatinous material in bottom of tube.	All surfaces dulled and tarnished except cut ones; gelatinous material in bottom of tube.	Some gelatinous material in bottom of tube; liquid phase is clear and water white; cut surfaces very shiny.

3.1.2. Specific Conductance Measurements

Specific conductance-concentration data for NaClO_4 solutions in propylene carbonate were obtained. This salt was chosen for study because of the relatively higher solubility (in water) of NaF compared to LiF . Assuming that this trend holds in PC, the dissolution of CuF_2 could be expected to be suppressed by substituting NaClO_4 for LiClO_4 as the electrolyte salt.

Sodium perchlorate showed a higher maximum conductivity than LiClO_4 , which was included in the test for comparison (6.8×10^{-3} mho/cm compared to 5.2×10^{-3} mho/cm). The specific conductance-concentration relationships for the two salts in PC are given in Figure 1, page 7.

The specific conductance-concentration data for LiClO_4 in dimethyl formamide were also obtained and are shown in Figure 2, page 8. In previous tests, spectroquality DMF showed poor stability toward metallic lithium; however, this solvent is to receive further evaluation after redistillation and/or other purification to see if it may be applicable in the 1-10 hour battery.

FIGURE I.

Specific Conductance of
 LiClO_4/PC and
 NaClO_4/PC
Temperature: 24.3°C

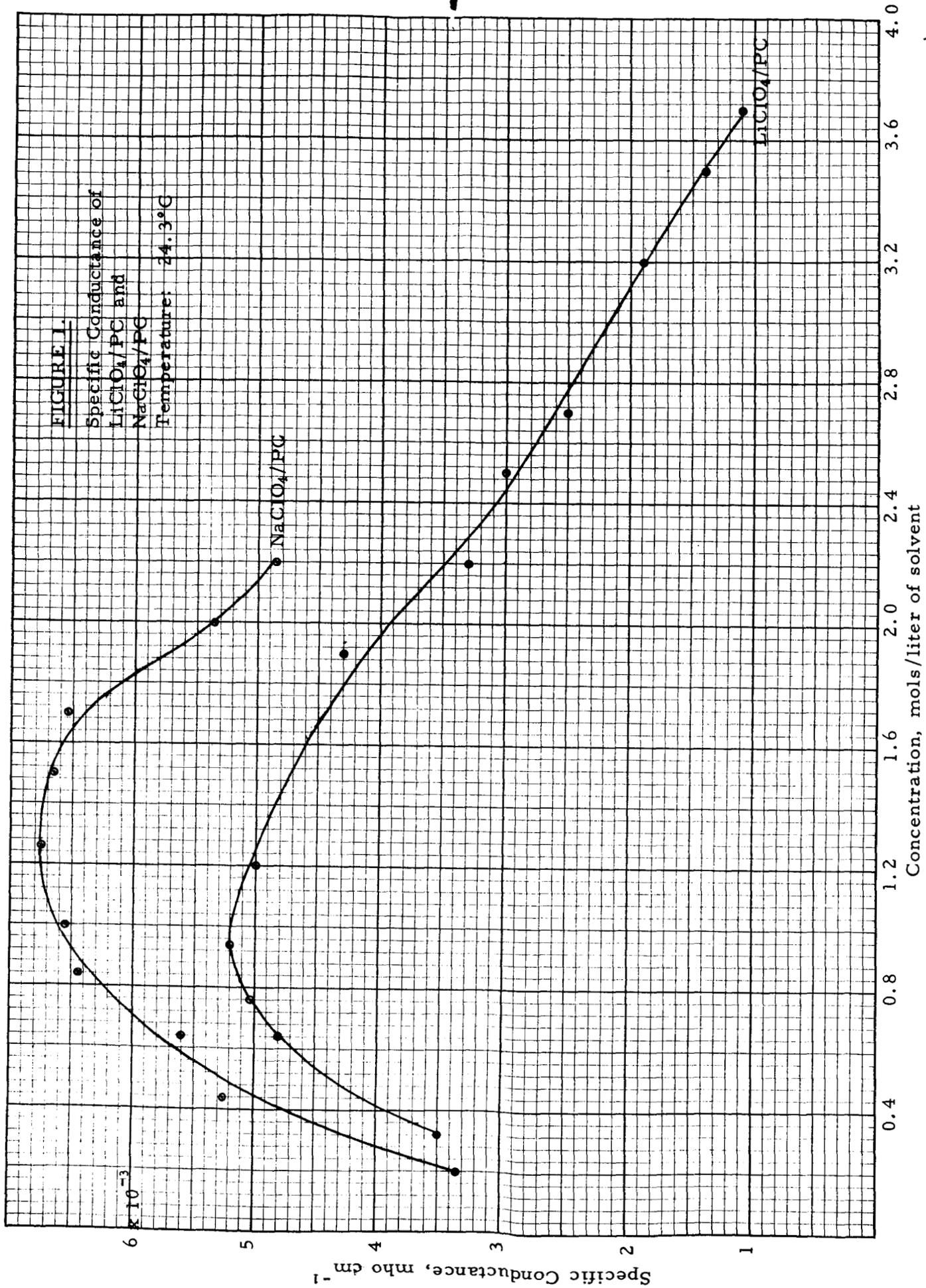
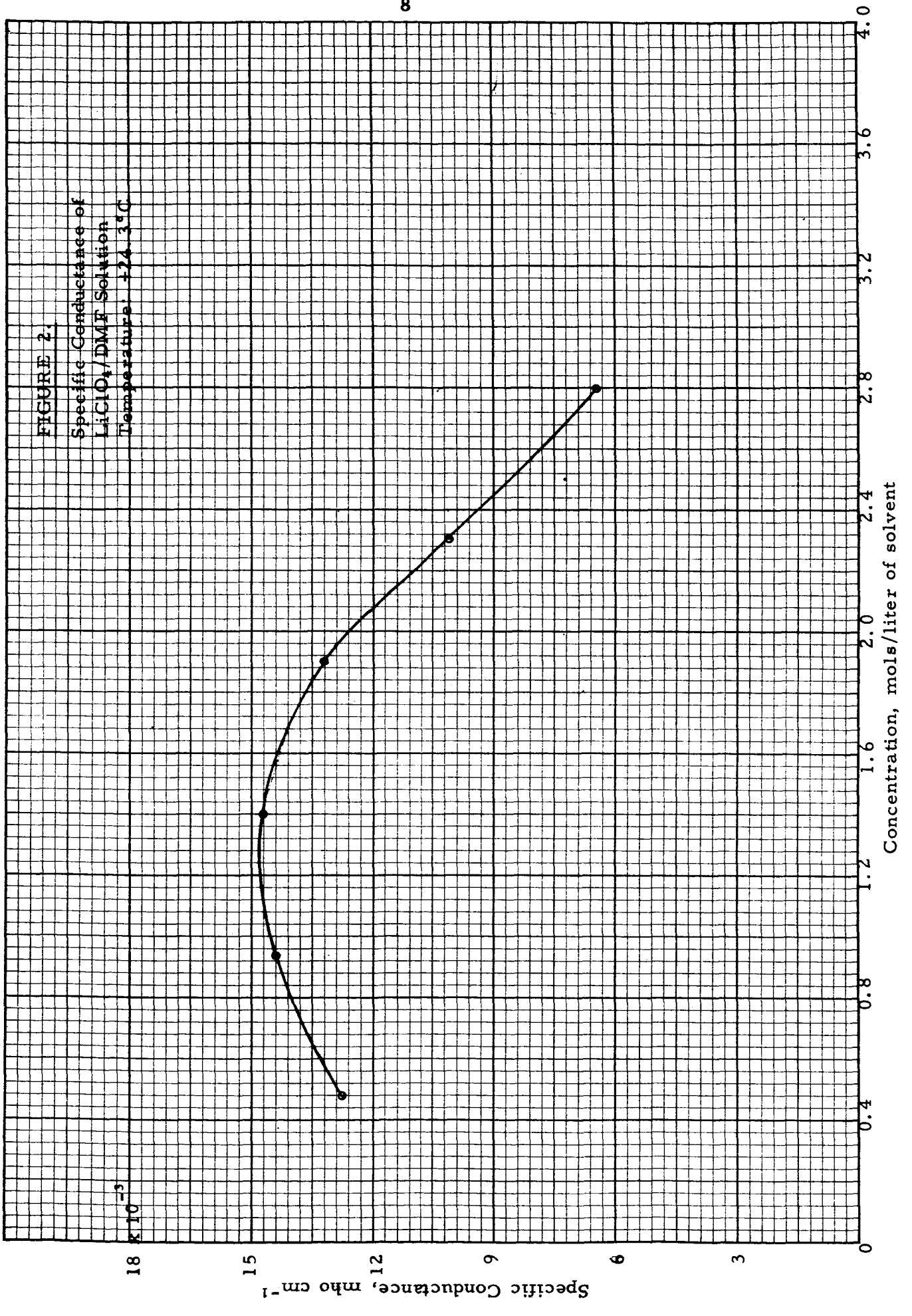


FIGURE 2:
Specific Conductance of
LiClO₄/DMF Solution
Temperature: +24.3°C



3.1.3. Vapor Pressure of LiClO₄-Methyl Formate Electrolyte

The vapor pressure of a 4.7M LiClO₄ in methyl formate solution was determined in order to obtain an estimate of what type of case construction may be employed for a methyl formate electrolyte battery. The solution was placed in a sealed glass tube equipped with a pressure gauge, and heated in a water bath. In order to test the apparatus for proper operation, the vapor pressure of the pure solvent was measured first and compared to data in the literature.*

Results of the vapor pressure determination are listed below.

TABLE II
VAPOR PRESSURE OF LiClO₄-MF ELECTROLYTE

Gauge Pressure, Atm. Abs.

Temperature °C	Solvent		4.7M LiClO ₄ Solution
	Literature	Test	
52	2.0	---	1.2
58	2.5	2.4	---
63	2.9	---	1.5
72	3.8	---	1.7

As expected, substantial reduction in vapor pressure has resulted in the 4.7M LiClO₄ solution compared to the pure solvent. The approximately 10 psig pressure at 72°C would not appear to be prohibitive for the construction of a light weight battery case for this system.

*Lange's Handbook of Chemistry, 6th Ed., page 1416.

3.2. POSITIVE ELECTRODE STUDIES

3.2.1. CuF_2 Solubility Studies

The studies of CuF_2 solubility in propylene carbonate and butyrolactone electrolytes described previously (NASA CR-54920) were completed during the past quarter. The solvents (propylene carbonate and butyrolactone) were prepared by agitating with excess amounts of lithium powder until no further hydrogen pressure was produced; at this point, the residual water in both solvents was below the sensitivity of the Karl Fischer test (20 ppm). The lithium treatment was followed by distillation, rejecting the first and last 10 volume percent of the distillate.

The lithium perchlorate used in these tests was vacuum-dried at 110°C for 24 hours, and water content (Karl Fischer analysis) was approximately 600 ppm. Anhydrous CuF_2 was used as received from Ozark Mahoning Company. X-ray analysis of this material showed the water level in this material to be about 0.33 percent (3300 ppm).

A series of 60 ml serum bottles equipped with hermetic stoppers were filled with 40 ml of solvent, 1.0g of CuF_2 , and 4.0, 8.0, or 12.0 grams of LiClO_4 . Distilled water was added to the bottles in quantities designed to produce water contamination levels in the range of 150 to 5000 ppm. The samples were agitated on a laboratory shaker with appropriately timed interruptions to allow the solid phase to settle. The samples were then compared for color, and the concentration of Cu^{++} in solution was determined by the thiosulphate titration.

Results of the copper ion determinations and the observed solution colors are listed in Tables III and IV, pages 12 and 15. The solutions which had the lower water contamination levels can be seen to have reached equilibrium at between 650 and 1000 hours of agitation, while those with the higher water levels still appeared to increase in copper concentration.

At equal LiClO_4 concentration, increasing water content increased the copper concentration in the solution. For example, increasing water content from 180 ppm to 5000 ppm increased the copper concentration after 1000 hours of agitation from 710 ppm to 7300 ppm. At approximately equivalent water contents, solubility of CuF_2 was more pronounced in the solutions having the higher LiClO_4 concentrations. However, the effect of LiClO_4 on the solubility of CuF_2 was much less pronounced than that of water contamination level. The solubility of CuF_2 was also found to be larger in butyrolactone than in propylene carbonate electrolyte.

The above results further demonstrate the need for very low water concentration in the CuF_2 -Li system in order to minimize loss of capacity during wet shelf life of the cells. The solubility tests may prove of value for evaluation of CuF_2 drying methods, since the X-ray examination is of limited utility where low water contents are encountered. To make this approach practical, a method for decreasing the time required for the analysis would have to be developed.

TABLE III

SOLUBILITY OF CuF_2 IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled;
 $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
 Lithium Perchlorate, Foote Mineral Co., vacuum dried at
 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
 Cupric Fluoride, Ozark Mahoning Co., as received;
 $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
 Distilled Water, Sunbeam Water Co.

Series A — 10 gm. LiClO_4 /100 ml PC; Solution Density = 1.25 gm/ml.

Water Content, ppm	Agitation Time, Hours	Copper (II) Concentration		Solution Color
		μ moles/ml	ppm	
120	25	2.5	125	Off White
	125	6.6	335	Off White
	290	7.0	355	Off White
	650	12.5	635	Light Tan
	1000	12.5	635	Tan
400	25	5.5	280	Off White
	125	7.0	355	Off White
	290	11.5	585	Off White
	650	14.2	720	Light Tan
	1000	15.0	765	Tan
810	25	6.0	305	Off White
	125	11.0	560	Off White
	290	15.7	800	Off White
	650	20.0	1015	Light Yellow Green
	1000	25.0	1270	Yellow Green
2220	25	18.0	915	Light Green
	125	32.5	1650	Light Green
	290	40.0	2030	Olive Green
	650	40.0	2030	Olive Green
	1000	52.0	2640	Olive Green
6050	25	101	5100	Blue Green
	125	113	5750	Green
	290	118	6000	Green
	650	145	7400	Green
	1000	175	8900	Green

TABLE III (Continued)

SOLUBILITY OF CuF_2 IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled;
 $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
 Lithium Perchlorate, Foote Mineral Co., vacuum dried at
 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
 Cupric Fluoride, Ozark Mahoning Co., as received;
 $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
 Distilled Water, Sunbeam Water Co.

Series B - 20 gm. LiClO_4 /100 ml PC; Solution Density = 1.30 gm/ml.

Water Content, <u>ppm</u>	Agitation Time, <u>Hours</u>	<u>Copper (II) Concentration</u>		Solution Color
		<u>μ mols/ml</u>	<u>ppm</u>	
150	25	4.6	224	Off White
	125	6.2	303	Off White
	290	6.5	317	Off White
	650	12.5	610	Light Tan
	1000	13.0	635	Light Tan
430	25	5.0	245	Off White
	125	6.8	333	Off White
	290	9.5	465	Off White
	650	17.5	855	Tan
	1000	17.0	830	Tan
960	25	4.7	230	Off White
	125	8.5	416	Off White
	290	15.6	765	Off White
	650	25.0	1220	Olive Yellow
	1000	24.5	1200	Olive Yellow
1760	25	4.8	235	Off White
	125	24.6	1210	Very Light Green
	290	36	1770	Light Green
	650	39.0	1900	Olive Green
	1000	38.8	1890	Olive Green
4960	25	32	1570	Light Blue Green
	125	90	4400	Green
	290	100	4890	Green
	650	135	6600	Green
	1000	135	6600	Green

TABLE III (Continued)

SOLUBILITY OF CuF_2 IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled;
 $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
 Lithium Perchlorate, Foote Mineral Co., vacuum dried
 at 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
 Cupric Fluoride, Ozark Mahoning Co., as received;
 $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
 Distilled Water, Sunbeam Water Co.

Series C — 30 gm. $\text{LiClO}_4/100$ ml PC; Solution Density = 1.34 gm/ml.

Water Content, ppm	Agitation Time, Hours	Copper (II) Concentration		Solution Color
		μ moles/ml	ppm	
180	25	4.9	232	Off White
	125	7.8	370	Off White
	290	9.4	446	Off White
	650	15.5	735	Light Tan
	1000	15.0	710	Light Tan
430	25	4.5	214	Off White
	125	7.8	370	Off White
	290	11.0	525	Off White
	650	17.5	830	Tan
	1000	17.5	830	Tan
980	25	4.5	214	Off White
	125	9.4	446	Off White
	290	15.5	740	Very Light Green
	650	25.0	1185	Olive Yellow
	1000	24.5	1160	Olive Yellow
2000	25	5.2	247	Off White
	125	32.0	1530	Very Light Green
	290	29.0	1860	Light Green
	650	50.0	2370	Olive Green
	1000	49.0	2320	Olive Green
5000	25	70	3330	Light Green
	125	104	5000	Green
	290	121	5800	Green
	650	155	7300	Green
	1000	155	7300	Green

TABLE IV

SOLUBILITY OF CuF_2 IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li dried and distilled;
 $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
 Lithium Perchlorate, Foote Mineral Co., vacuum dried at
 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
 Cupric Fluoride, Ozark Mahoning Co., as received;
 $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
 Distilled Water, Sunbeam Water Co.

Series A — 10 gm. LiClO_4 /100 ml BL; Solution Density = 1.18 gm/ml.

Water Content, ppm	Agitation Time, Hours	Copper (II) Concentration		Solution Color
		$\mu\text{moles/ml}$	ppm	
120	25	5.9	305	Off White
	125	8.4	435	Off White
	290	12.6	655	Pale Yellow
	650	14.7	790	Yellow Green
	1000	14.5	780	Yellow Green
430	25	4.0	215	Off White
	125	4.5	240	Off White
	290	10.0	540	Pale Yellow
	650	14.0	755	Yellow Green
	1000	18.5	995	Light Olive
850	25	5.0	270	Off White
	125	8.8	475	Very Light Green
	290	17.9	965	Light Yellow Green
	650	22.7	1220	Yellow Green
	1000	29.0	1560	Olive
2340	25	18.0	970	Light Green
	125	31.0	1670	Green
	290	53.0	2850	Green
	650	90	4850	Green
	1000	115	6180	Green
6440	25	113	6100	Blue Green
	125	125	6730	Blue Green
	290	162	8700	Dark Green
	650	226	12200	Emerald Green
	1000	285	15300	Emerald Green

TABLE IV (Continued)

SOLUBILITY OF CuF_2 IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li dried and distilled;
 $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
 Lithium Perchlorate, Foote Mineral Co, vacuum dried at
 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
 Cupric Fluoride, Ozark Mahoning Co., as received;
 $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
 Distilled Water, Sunbeam Water Co.

Series B — 20 gm. $\text{LiClO}_4/100$ ml BL; Solution Density = 1.22 gm/ml.

Water Content, ppm	Agitation Time, Hours	Copper (II) Concentration		Solution Color
		μ moles/ml	ppm	
160	25	4.8	250	Off White
	125	8.0	415	Pale Yellow
	290	15.0	785	Yellow Green
	650	21.4	1115	Olive Yellow
	1000	24.0	1250	Olive Yellow
460	25	5.6	290	Pale Yellow
	125	10.8	565	Pale Yellow Green
	290	21.2	1105	Yellow Green
	650	34.5	1800	Olive
	1000	40.5	2110	Olive
1020	25	8.0	415	Pale Yellow
	125	16.8	875	Yellow Green
	290	38.0	1980	Green
	650	60.0	3120	Olive Green
	1000	68.0	3540	Olive Green
1870	25	12.8	665	Pale Green
	125	54	2810	Green
	290	75.0	3910	Dark Green
	650	76.0	3960	Dark Green
	1000	120	6250	Dark Green
5260	25	73	3800	Green
	125	165	8600	Emerald Green
	290	230	12000	Emerald Green
	650	235	12200	Emerald Green
	1000	240	12500	Dark Emerald Green

TABLE IV (Continued)

SOLUBILITY OF CuF_2 IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li dried and distilled;
 $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
 Lithium Perchlorate, Foote Mineral Co., vacuum dried at
 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
 Cupric Fluoride, Ozark Mahoning Co., as received;
 $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
 Distilled Water, Sunbeam Water Co.

Series C — 30 gm. LiClO_4 /100 ml BL; Solution Density = 1.27 gm/ml.

Water Content, ppm	Agitation Time, Hours	Copper (II) Concentration		Solution Color
		μ moles/ml	ppm	
190	25	6.5	325	Pale Yellow
	125	10.9	545	Pale Yellow Green
	290	16.0	800	Yellow Green
	650	24.0	1200	Olive
	1000	27.5	1375	Olive
460	25	7.2	360	Light Yellow Green
	125	12.8	640	Light Yellow Green
	290	21.6	1080	Yellow Green
	650	27.0	1350	Olive Green
	1000	43.0	2150	Olive Green
1040	25	9.3	465	Light Yellow Green
	125	23.6	1180	Light Green
	290	39.0	1960	Green
	650	50.0	2500	Olive Green
	1000	84.0	4200	Dark Olive Green
2100	25	16.9	845	Yellow Green
	125	70	3500	Green
	290	79.0	3960	Dark Green
	650	89.5	4480	Dark Green
	1000	135	6750	Dark Green
5250	25	64	3200	Green
	125	177	8860	Emerald Green
	290	215	10750	Emerald Green
	650	250	12500	Dark Emerald Green
	1000	250	12500	Dark Emerald Green

3.2.2. Copper Fluoride Drying Studies

The removal of trace water from CuF_2 has been of major importance on this program, since the detrimental effect of water on the properties of CuF_2 has been repeatedly demonstrated. The main effect of presence of water appears to be the increased dissolution of the CuF_2 in the electrolyte which results in poor cell performance after wet stand at normal temperature.

Two basic procedures have been employed in this laboratory for the removal of water from CuF_2 . The first method involves heating of the material under vacuum, while the second consists of placing the material in a vertical tube heated by a constant temperature bath and continuously purging the tube with dry argon.

To study the effect of the various drying conditions, eight batches of anhydrous CuF_2 were treated. The method of treatment and the X-ray patterns obtained before and after drying are presented in Table V, page 19. The relative concentration of each material in the sample is proportional to the peak intensity (counts/second), but the actual percentage figures can only be calculated for the materials which are available in pure form for calibration (CuF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$).

It can be seen from an examination of Table V, page 19, that the main decomposition products which result from heating the salt are $\text{CuOHF} \cdot \text{CuF}_2$ and CuOHF . An unknown compound having a major peak intensity at 4.15 Å is also produced. This material increases in quantity with increasing drying time and also with increasing temperature.

3. 2. 3. Decomposition of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

Since decomposition of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ is of importance in removing water from CuF_2 , this reaction was studied further in a series of decomposition tests performed on the dihydrate. In the first series of experiments, 50 grams of dihydrate were heated in a sealed vacuum oven having a volume of 6.5 L from which air was evacuated prior to application of heat. Results of the X-ray analyses of the initial and resulting materials are given in Table VI, page 21.

A second series of tests was performed by heating the dihydrate in a tube while purging with argon as described in the previous section; results of these runs are presented in Table VII, page 22.

It can be seen from the X-ray data that the main decomposition products obtained by both methods are CuOHF and an unknown compound having a major peak intensity at 4.15 Å, the latter becoming more predominant with longer decomposition time and higher temperature.

Further work under more closely defined conditions is necessary in order to clarify the nature of the decomposition reactions involved. It is of interest to note, however, that preliminary tests indicate a low solubility of the "unknown" decomposition product of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ in LiClO_4 -PC electrolyte compared to dried CuF_2 . The properties of this unknown compound will be studied further to see if an advantage could be gained by utilizing it as the positive active material of the cell in place of CuF_2 .

TABLE VI
 DECOMPOSITION OF $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, LOT A, SEALED CHAMBER

Sample No.	$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, Lot A Untreated	44-1	B54-1	55-7				
Time		32 Hrs.	20 Hrs.	20 Hrs.				
Temperature		150°C	150°C	135°C				
Chamber Pressure		Vacuum*	0.1 Atm. abs.	1 Atm. abs.				
Compound	"D" Value A	Relative Intensity	Counts/ Second	Relative Intensity	Counts/ Second	Relative Intensity	Counts/ Second	Relative Intensity
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	4.78	100	2400	100	24	256	100	
	3.71	25	600	25	-----	-----	---	
	2.71	45	1080	45	320	**	---	
$\text{CuOHF} \cdot \text{CuF}_2$	4.22	100	-----	---	-----	320	---	
	3.54	85	-----	---	-----	-----	---	
	3.45	70	-----	---	68	392	---	
CuOHF	4.68	100	-----	---	2496	1584	100	
	2.55	40	-----	---	1044	768	48	
	1.97	35	-----	---	576	352	22	
Unknown Material	4.15	---	-----	---	1136	-----	---	
	2.77	---	-----	---	560	-----	---	
	2.75	---	-----	---	320	-----	---	

* Vacuum pump was connected to chamber for 16 hours at which time chamber was sealed.

** Line is obscured by CuOHF line.

TABLE VII

DECOMPOSITION OF $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, LOT B, ARGON SWEEP

Sample No.	$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, Lot B Untreated	55-9	57-1	59-5				
Time		50 Hrs.	15 Hrs. 10 Hrs.	20 Hrs.				
Temperature		135°C	150°C + 165°C	185°C				
Compound	"D" Value	Relative Intensity	Counts/Second	Relative Intensity	Counts/Second	Relative Intensity	Counts/Second	Relative Intensity
	A							
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	4.78	100	1696	100	-----	-----	-----	-----
	3.71	25	464	27	-----	-----	-----	-----
	2.71	45	800	47	-----	-----	-----	-----
$\text{CuOHF} \cdot \text{CuF}_2$	4.22	100	124	100	-----	-----	328	100
	3.54	85	124	100	-----	-----	264	80
	3.45	70	100	81	-----	-----	164	50
CuOHF	4.68	100	100	100	2272	1360	344	100
	2.55	40	64	64	1008	672	224	65
	1.97	35	76	76	424	232	80	23
Unknown Material	4.15	---	---	---	128	448	370	100
	2.77	---	---	---	56	308	180	49
	2.75	---	---	---	46	172	---	---

3.3. CELL SYSTEMS STUDIES

3.3.1. Ag_2O_2 -Li Cell Tests

Since the solubility of CuF_2 in LiClO_4 -PC electrolyte appears to contribute adversely to the wet stand capability of the CuF_2 -Li cells, self-discharge tests with cells having Ag_2O_2 instead of CuF_2 in the positive electrode were initiated. The silver oxide was chosen for the tests because it was presumed to have a very low solubility in the electrolyte, thus allowing evaluation of the remaining cell construction for wet stand capability without the complication of a dissolved species (Cu^{++}) attacking the lithium electrode from solution.

In order to study the wet stand capability of the Ag_2O_2 -Li system, six cells with LiClO_4 -PC electrolyte were constructed and tested. Two cells were discharged through 200 Ω loads (ca. 0.5 mA/cm²), while the remaining four cells had wet stands of two and four weeks at 35°C. Construction and discharge data for the cells are summarized in Table VIII, page 24, and voltage-time data for Cells 1, 2, and 4 are plotted in Figure 3, page 25.

Degradation of capacity even after two weeks of stand at 35°C was quite severe and approximately comparable to that observed in CuF_2 -Li cells. However, appearance of the lithium electrodes at the end of the test was comparatively very good, with no visible deposits on the surface. The free electrolyte level in the cells as viewed through the transparent polyethylene envelope had completely disappeared after the wet stand period; this condition could easily have affected the discharge performance of the cells. The above tests are scheduled to be repeated in a hermetically sealed test assembly in order to minimize electrolyte loss during open circuit stand and discharge.

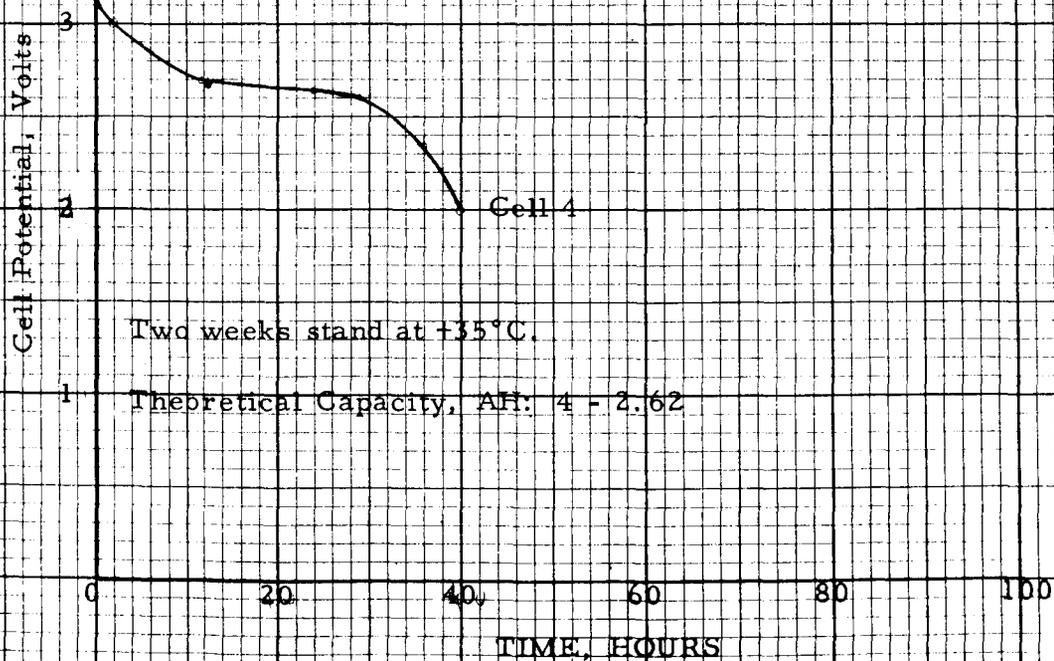
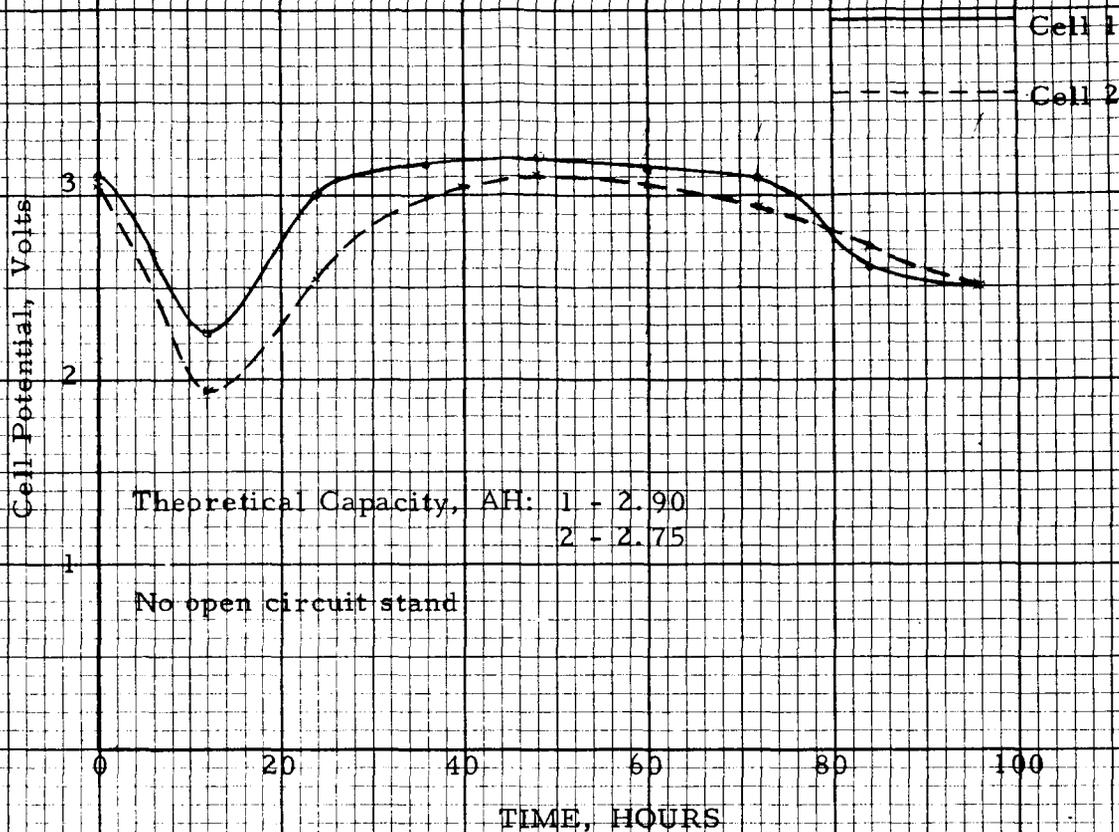
TABLE VIII
SELF-DISCHARGE IN Ag_2O_2 -Li CELLS
WITH LiClO_4 -PC ELECTROLYTE

Stand Temperature: 35°C
 Discharge Temperature: 35°C
 Load: 200 ohms

Cell No.	Stand Time, Weeks	Theoretical Ag_2O_2 Cap. AH *	Hours to 2.5 VF	Capacity to 2.5 VF AH	Average Discharge Potential Volts	Cathode Eff. %
8-1	-	2.90	86	1.25	2.89	43
8-2	-	2.75	92	1.14	2.48	42
8-3	2	2.88	4	----	----	--
8-4	2	2.62	30	0.41	2.75	16
8-5	4	2.66	3	----	----	--
8-6	4	2.44	3	----	----	--

* Based on 100% Ag_2O_2 in active material.

Test No. 640-8
 Load: 200 ohms
 Temperature: +35°C
 Electrolyte: 15 gm LiClO_4 /100 ml PC.



PERFORMANCE OF Ag_2O_2 -Li CELLS
 FIGURE 3.

3.3.2. Self Discharge Tests in Propylene Carbonate

Further evaluation of the wet stand capability of CuF_2 -Li cells with propylene carbonate electrolyte was conducted during the past quarter. The main variable under study was the water content of the CuF_2 used in constructing the positive electrodes. One lot of CuF_2 was dried with argon at 130°C for 16 hours, and a second lot was dried under the same conditions for 113 hours. Subsequent X-ray analysis of the treated materials indicated water contents of below 0.3 and below 0.1 percent, respectively.

Copper fluoride test electrodes were constructed by the filter mat technique employed in previous self discharge tests (CuF_2 : 82 percent, graphite: 12 percent, paper fiber: 6 percent, 29 cm^2 geometric electrode area, 4-5 AH theoretical capacity). Three-plate cells with lithium sheet electrodes and 0.03 inch microporous rubber separation were constructed and filled with propylene carbonate electrolyte (15g LiClO_4 /100 ml PC). Cells were discharged thru $200\ \Omega$ resistors at 35°C immediately after filling with electrolyte, and after wet stand at 35°C and -15°C .

Without open circuit stand period, capacity was somewhat higher for the cells which had CuF_2 dried for the shorter period (16 hours), indicating that some decomposition of CuF_2 may have taken place during the drying period. After a two-week stand at 35°C , only two of the six cells with each type of CuF_2 had any significant capacity above 2.5 volts. After stand periods of 2, 4, and 6 weeks at -15°C , cell performance was not significantly different than had been obtained from cells which had received no open circuit stand. Results of the discharge tests are summarized in Tables IX and X, pages 27 and 28. The voltage-time data for the cells are presented in Figures 4 to 8, pages 29 and 33, and the extent of self discharge under the various test conditions for the highest performance cell in each group is displayed graphically in Figure 9, page 34.

Inspection of the cells at the end of test did not reveal clearly why the cells failed to discharge after the open circuit stand period at 35°C . All cell components appeared to be in good condition, and no evidence of short-circuiting could be found. However, the unabsorbed portion of the electrolyte had disappeared during the stand period, and an ester-like odor was always evident in the constant temperature chamber. This suggests loss of solvent by decomposition and evaporation, which contributes to the loss of capacity after stand. Also, the loss of electrolyte is more pronounced in the cells which show more extensive capacity loss during stand. This factor will be studied further utilizing hermetically sealed cell assemblies.

TABLE IX

SELF-DISCHARGE IN CuF₂-Li CELLSCuF₂ Dried 16 Hours at 130°C under Argon

Cell No.	Stand Conditions		Theo. CuF ₂ Capacity, AH	Hours to 2.5 VF	Capacity to 2.5 VF, AH	Average Discharge Potential, Volts	Cathode Eff., %
	Temp. °C	Time, wks.					
1	---	--	3.72	170	2.64	3.10	71
2	---	--	3.98	201	3.16	3.14	79
3	---	--	3.93	108	1.65	3.06	42
4	---	--	4.18	184	2.85	3.09	68
5	+35	2	3.83	7	---	---	---
6	+35	2	3.39	0	---	---	---
7	+35	2	3.97	12	---	---	---
8	+35	2	3.80	18	0.25	2.76	7
9	+35	2	4.20	12	---	---	---
10	+35	2	4.04	42	0.59	2.81	15
11	-15	2	3.90	82	1.25	3.05	32
12 ²	-15	2	4.32	46	0.75	3.25	17
13	-15	4	3.52	141	2.16	3.06	61
14	-15	4	3.50	107	1.64	3.05	47
15 ¹	-15	6	4.00	---	---	---	---
16 ¹	-15	6	3.44	---	---	---	---

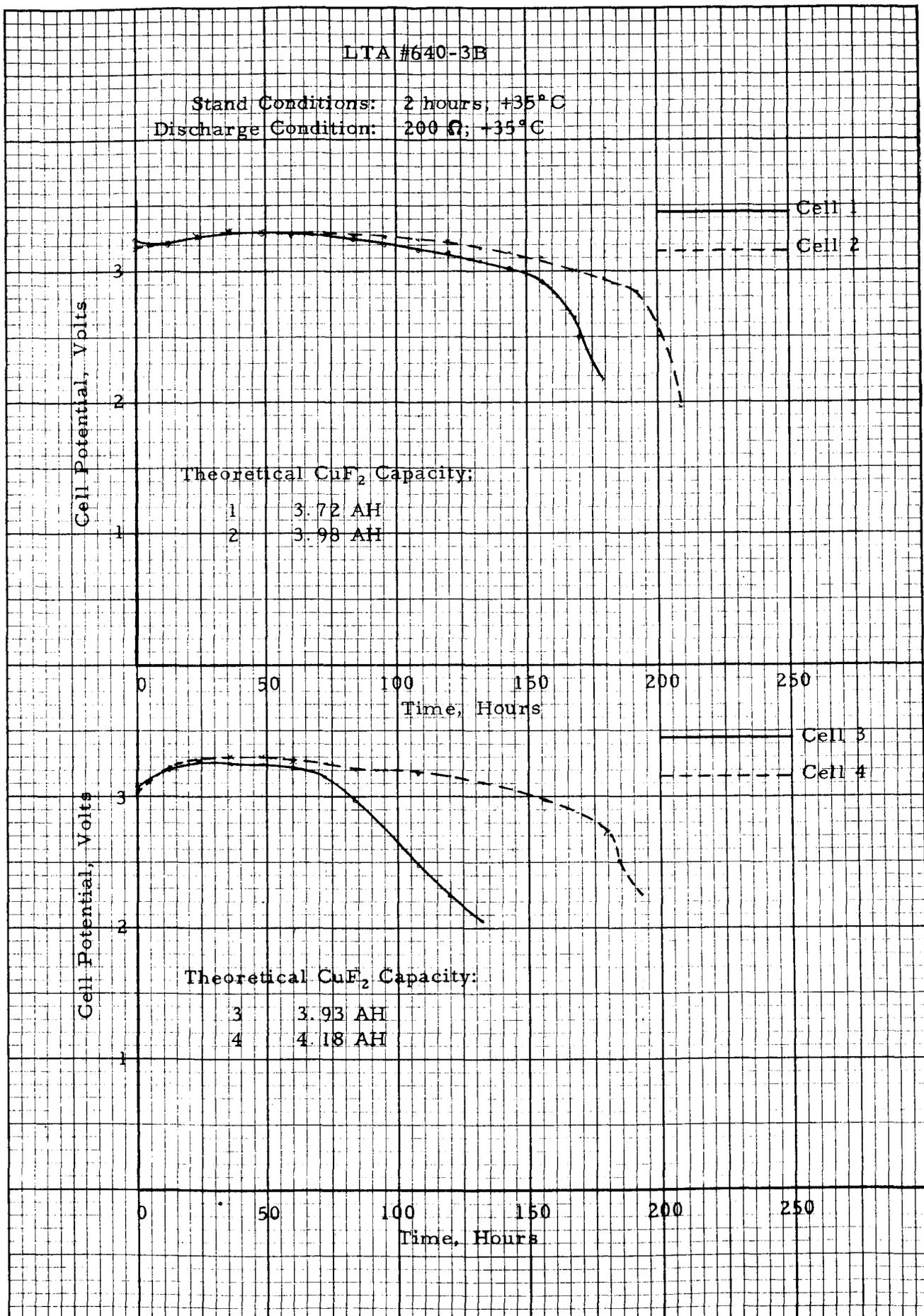
¹ Test in progress.² Cell had internal short circuit.

TABLE X

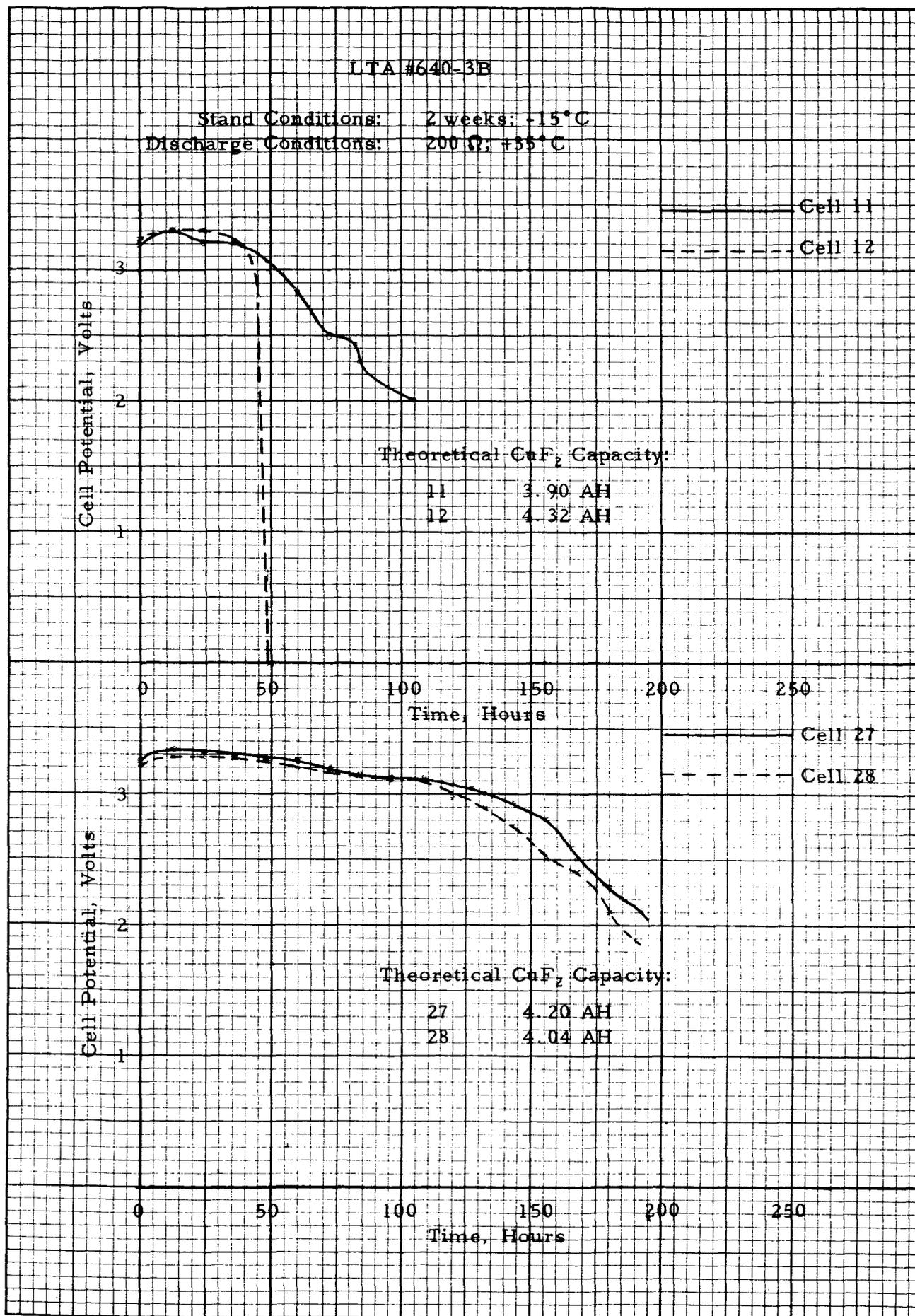
SELF-DISCHARGE IN CuF₂-Li CELLSCuF₂ Dried 113 Hours at 130°C under Argon

Cell No.	Stand Conditions		Theo. CuF ₂ Capacity, AH	Hours to 2.5 VF	Capacity to 2.5 VF, AH	Average Discharge Potential, Volts	Cathode Eff. %
	Temp. °C	Time, wks.					
17	---	--	4.67	170	2.64	3.10	57
18	---	--	4.58	170	2.50	2.94	55
19	---	--	4.77	202	3.15	3.11	66
20	---	--	4.24	122	1.80	2.94	42
21	+35	2	4.79	41	0.58	2.81	12
22	+35	2	4.42	2	---	---	---
23	+35	2	4.83	12	0.17	2.77	3
24	+35	2	4.84	0	---	---	---
25	+35	2	4.36	12	---	---	---
26	+35	2	4.58	12	---	---	---
27	-15	2	4.20	168	1.62	3.11	39
28	-15	2	4.04	156	2.40	3.07	59
29	-15	4	4.11	155	2.40	3.09	58
30	-15	4	4.27	173	2.65	3.05	62
31 ¹	-15	6	4.81	---	---	---	---
32 ¹	-15	6	4.62	---	---	---	---

¹ Test in progress.



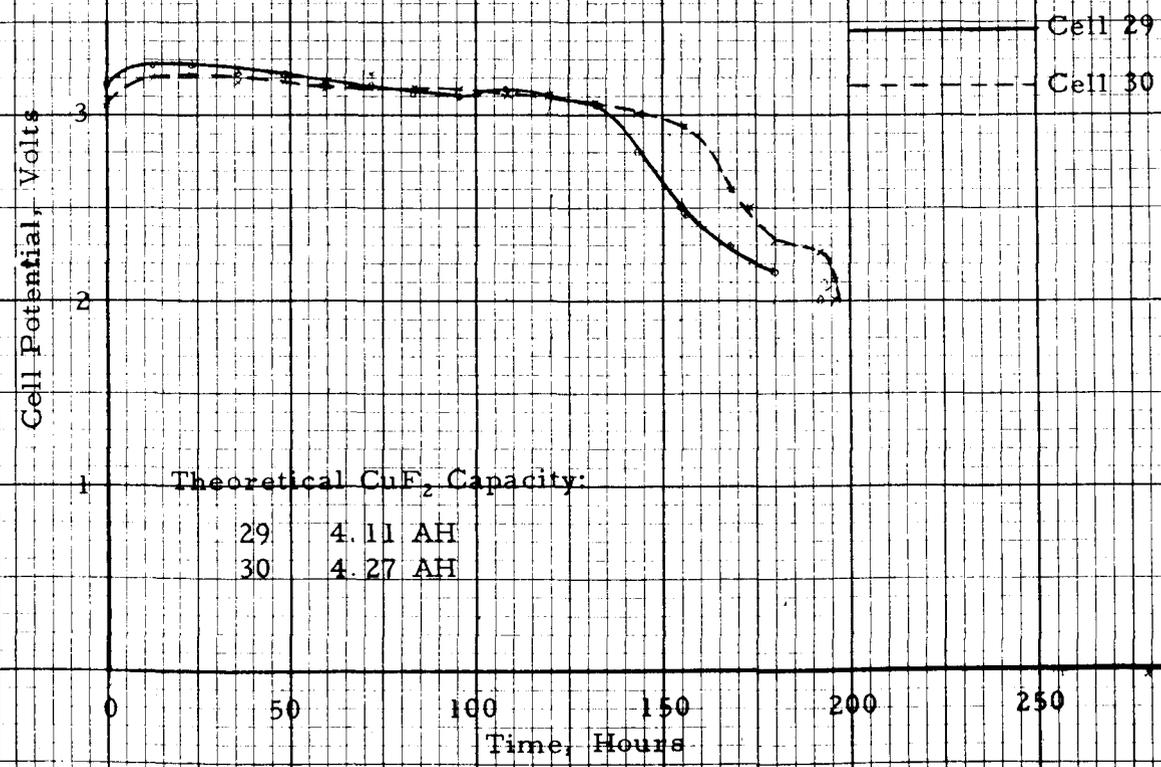
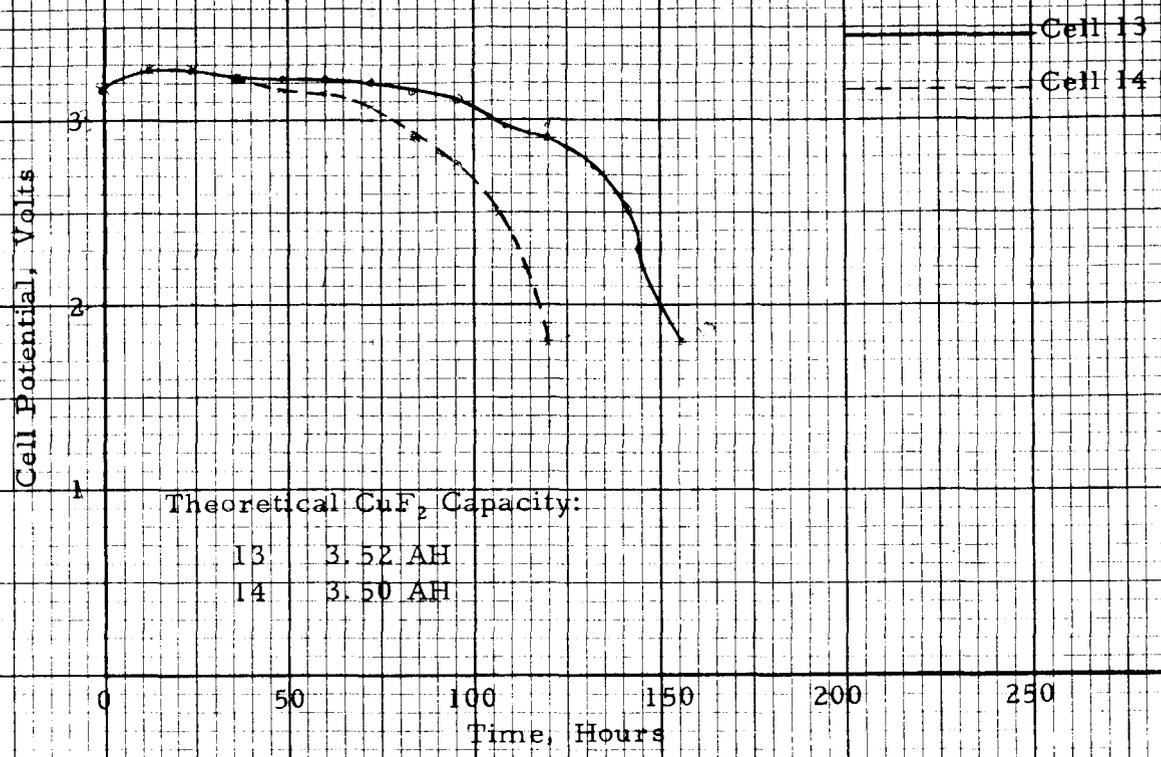
PERFORMANCE OF CuF_2 -Li CELLS
FIGURE 4



PERFORMANCE OF CuF_2 -Li CELLS
 FIGURE 5

LTA #640-3B

Stand Conditions: 4 weeks; +15°C
 Discharge Conditions: 200 Ω; +55°C



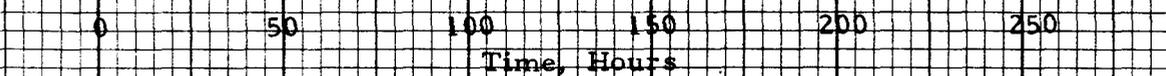
PERFORMANCE OF CuF₂-Li CELLS
 FIGURE 6

LTA #640-3B

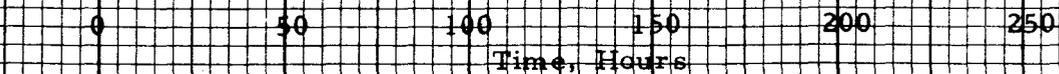
Stand Conditions: 6 weeks; -15°C
 Discharge Conditions: 200 Ω ; $+35^{\circ}\text{C}$

Theoretical CuF_2 Capacity:

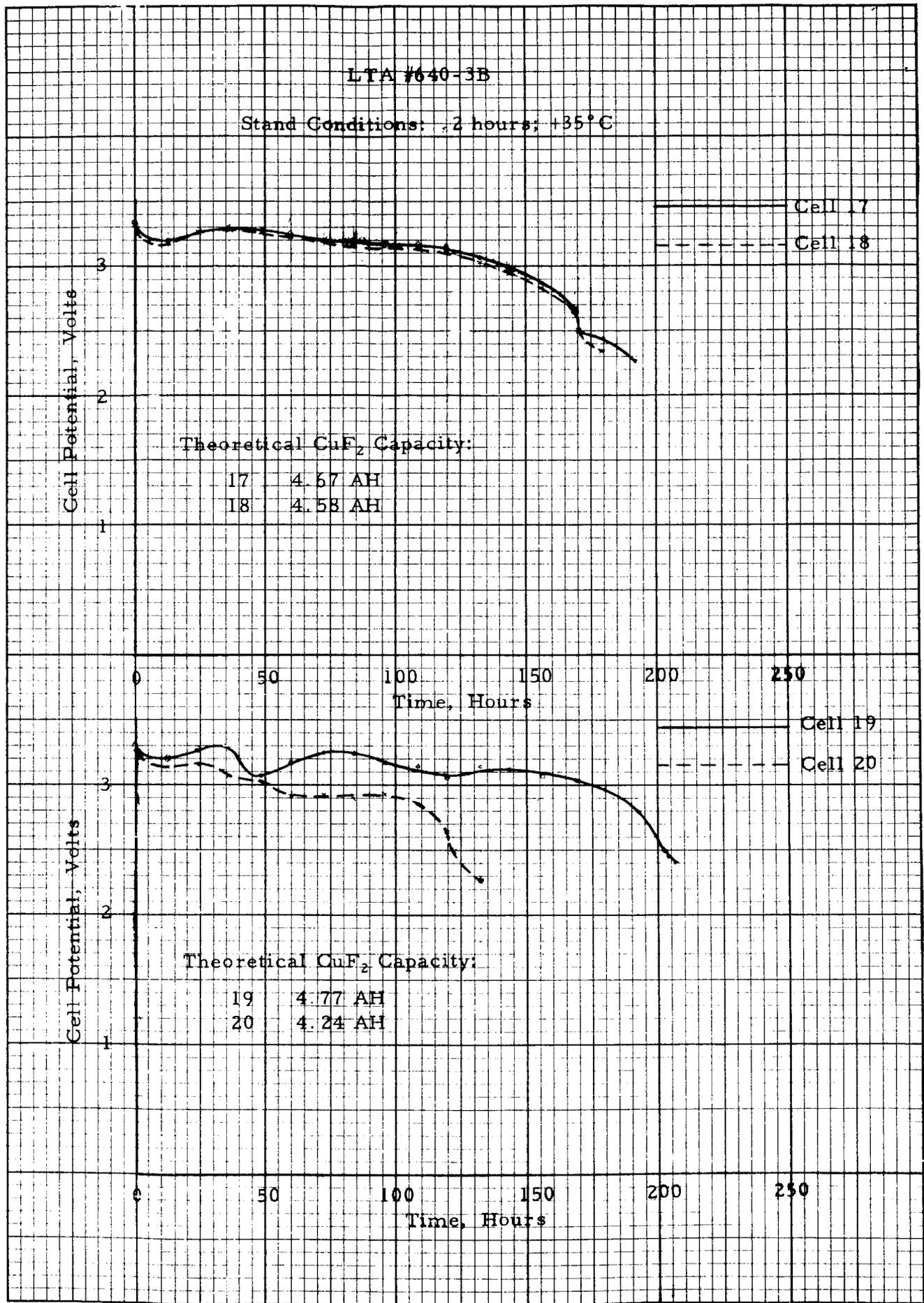
15	4.00 AH
16	3.44 AH

Theoretical CuF_2 Capacity:

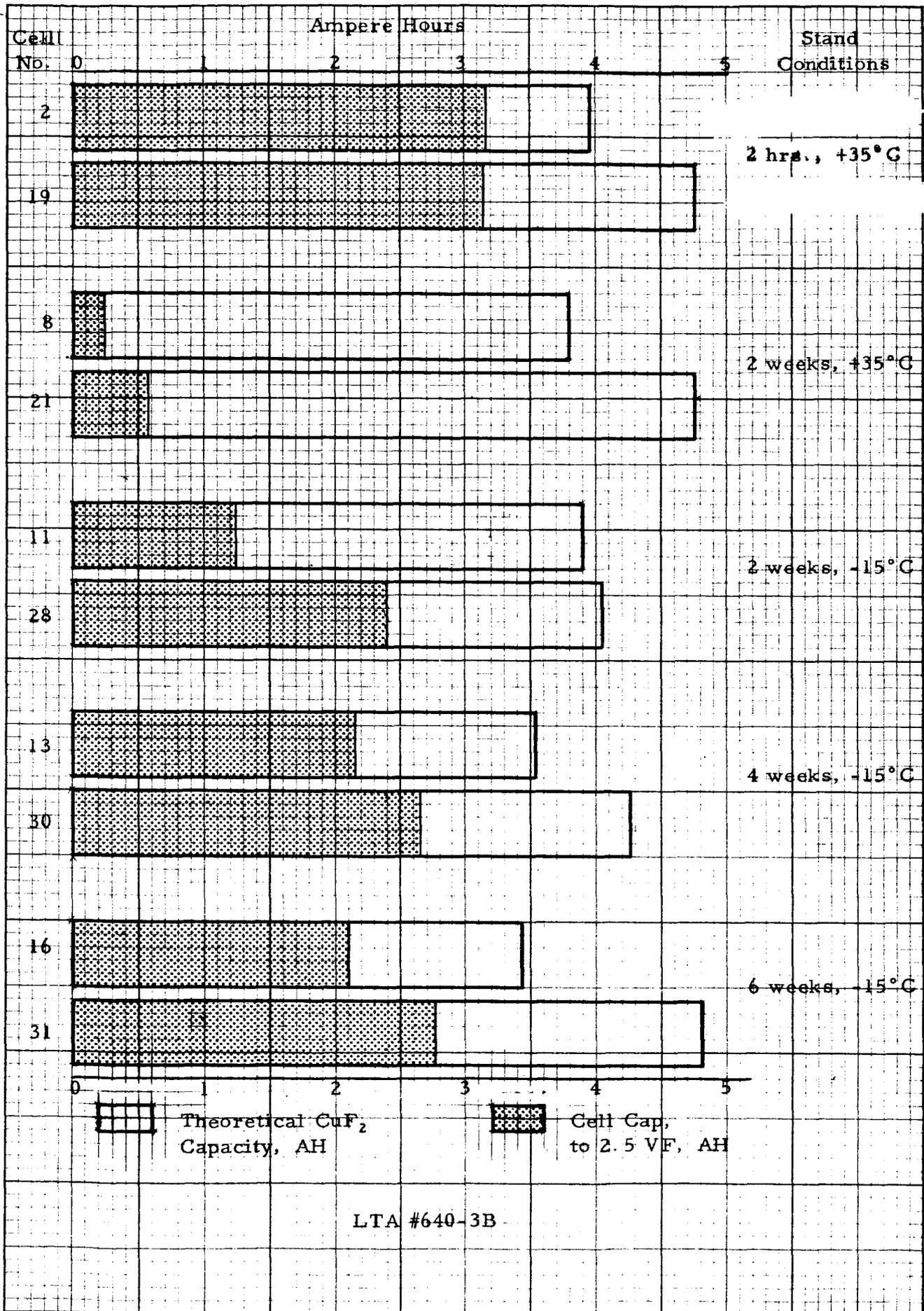
31	4.81 AH
32	4.62 AH



PERFORMANCE OF CuF_2 -Li CELLS
 FIGURE 7



PERFORMANCE OF CuF_2 -Li CELLS
FIGURE 8



SELF-DISCHARGE IN CuF_2 -Li CELLS
FIGURE 9

3.3.3. Butyrolactone Cell Tests

Butyrolactone had been tested during previous work on this program as a possible electrolyte solvent for CuF_2 -Li cells. It showed generally less desirable properties in compatibility and cell discharge tests compared to propylene carbonate. However, the solvent purity level in these earlier tests was not comparable to that presently obtained in PC. Since butyrolactone possesses certain desirable properties compared to propylene carbonate (higher specific conductance lower viscosity) it was decided to study cell performance with BL- LiClO_4 electrolyte having water content comparable to that presently obtained in PC- LiClO_4 electrolyte.

Test cells were assembled using the argon stream dried CuF_2 and cell construction described in Section 3.3.2. The butyrolactone electrolyte had a concentration of 15g LiClO_4 /100 ml solvent, and the water content as determined by Karl Fischer analysis was 150 ppm. The cells were discharged thru 200 Ω loads at 35°C after filling with electrolyte and after wet open circuit stand periods of one week at 35°C and two weeks at -15°C.

No capacity was retained by the four cells which experienced active stand at 35°C. Inspection of the components showed a large amount of copper colored deposit in the positive electrode matrix, although no evidence of short circuits thru the microporous rubber separation could be found. After the two-week stand period at -15°C, capacity was somewhat higher than without stand. Results of the discharge tests are summarized in Table XI, page 36, and voltage-time curves for some cells are given in Figures 10 to 12, pages 37 to 39.

The discharge performance of butyrolactone electrolyte cells was poor compared to similar cells having propylene carbonate electrolyte solvent. The CuF_2 reduction efficiency was only 20-30 percent compared to 60-80 percent obtained with propylene carbonate electrolyte. This reduction of efficiency is probably associated with the greater solubility of CuF_2 in butyrolactone electrolyte, although the exact mode of failure could not be determined from inspection of discharged cells. In view of the above results, no further tests with butyrolactone electrolyte are contemplated at this time.

TABLE XI

PERFORMANCE OF CuF_2 -Li CELLS
WITH BUTYROLACTONE ELECTROLYTE

Electrolyte: 15g LiClO_4 /100 ml BL
 Water Content: 150 ppm
 Discharge Temperature: 35°C
 Discharge Load: 200 Ω
 Electrode Area: 29 cm^2
 Separation: 0.03" MPR

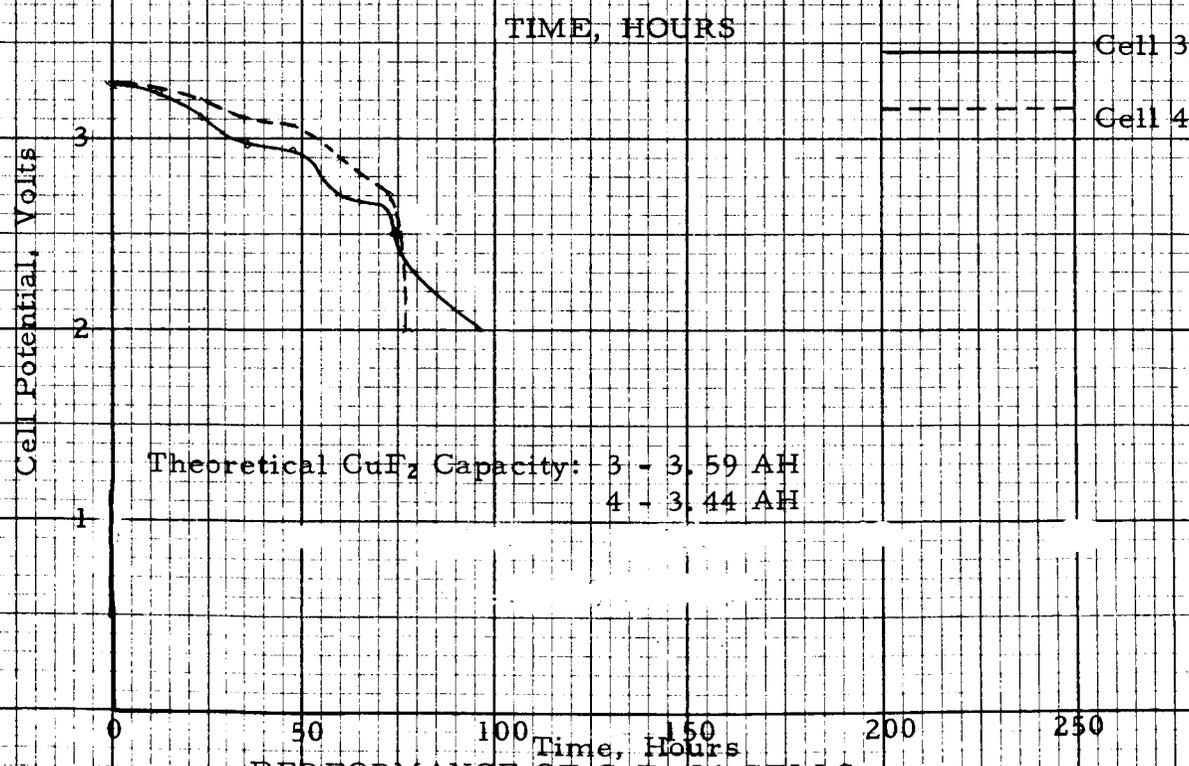
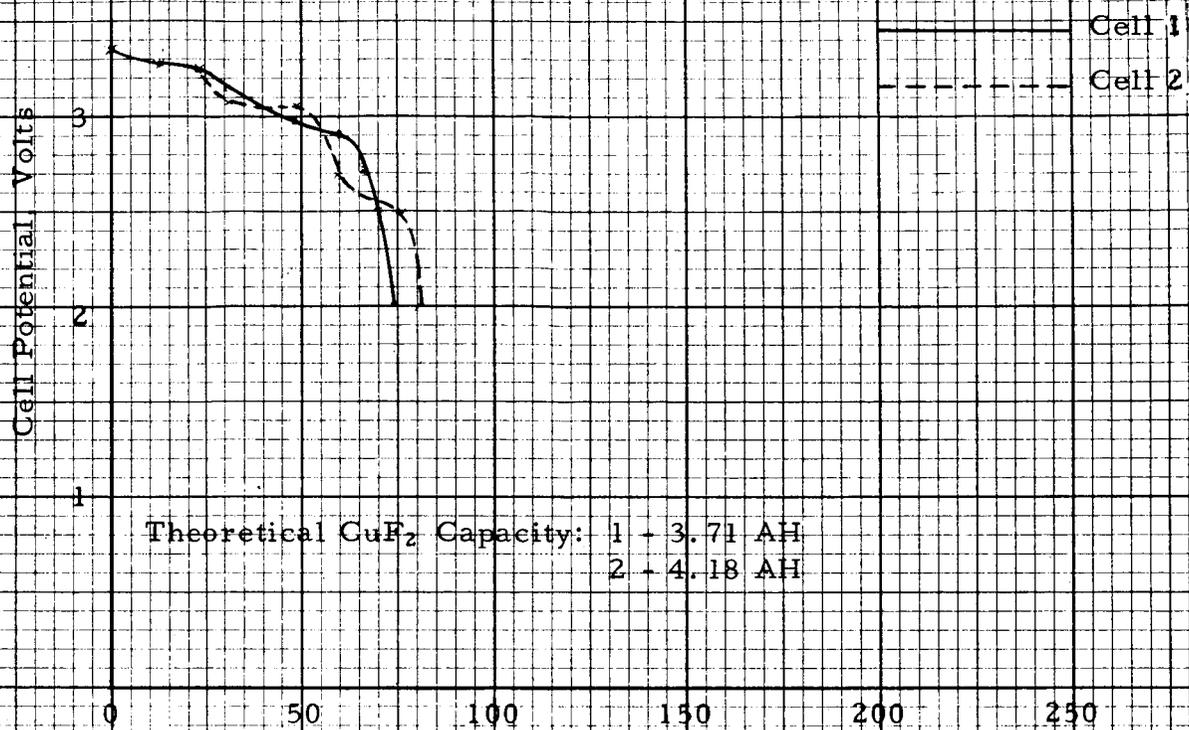
Cell No.	Stand Conditions		Theo. CuF_2 Capacity, AH	Hours to 2.5 VF	Capacity to 2.5 VF, AH	Average Discharge Potential, Volts	Percent Cathode Efficiency
	Temp. °C	Time, wks.					
1*	--	--	3.71	70	1.07	3.05	29
2*	--	--	4.18	76	1.17	2.99	28
3*	--	--	3.59	74	1.98	2.92	30
4*	--	--	3.44	75	1.16	3.01	34
9**	--	--	3.90	64	1.00	3.12	26
10**	--	--	4.50	70	1.10	3.13	24
11**	--	--	4.67	62	0.96	3.08	21
12**	--	--	4.60	59	0.93	3.13	20
5*	+35	1	3.92	\bar{D}	---	---	--
6*	+35	1	4.10	\bar{D}	---	---	--
13**	+35	1	4.82	\bar{D}	---	---	--
14**	+35	1	4.58	<1	---	---	--
7*	-15	2	4.26	118	1.80	3.05	42
8*	-15	2	4.12	90	1.36	3.03	33
15**	-15	2	4.62	95	1.45	3.06	31
16**	-15	2	4.71	97	1.45	3.00	31

¹ Open Circuit Voltage <1V after stand

* CuF_2 : Dried in argon for 16 hours at 130°C

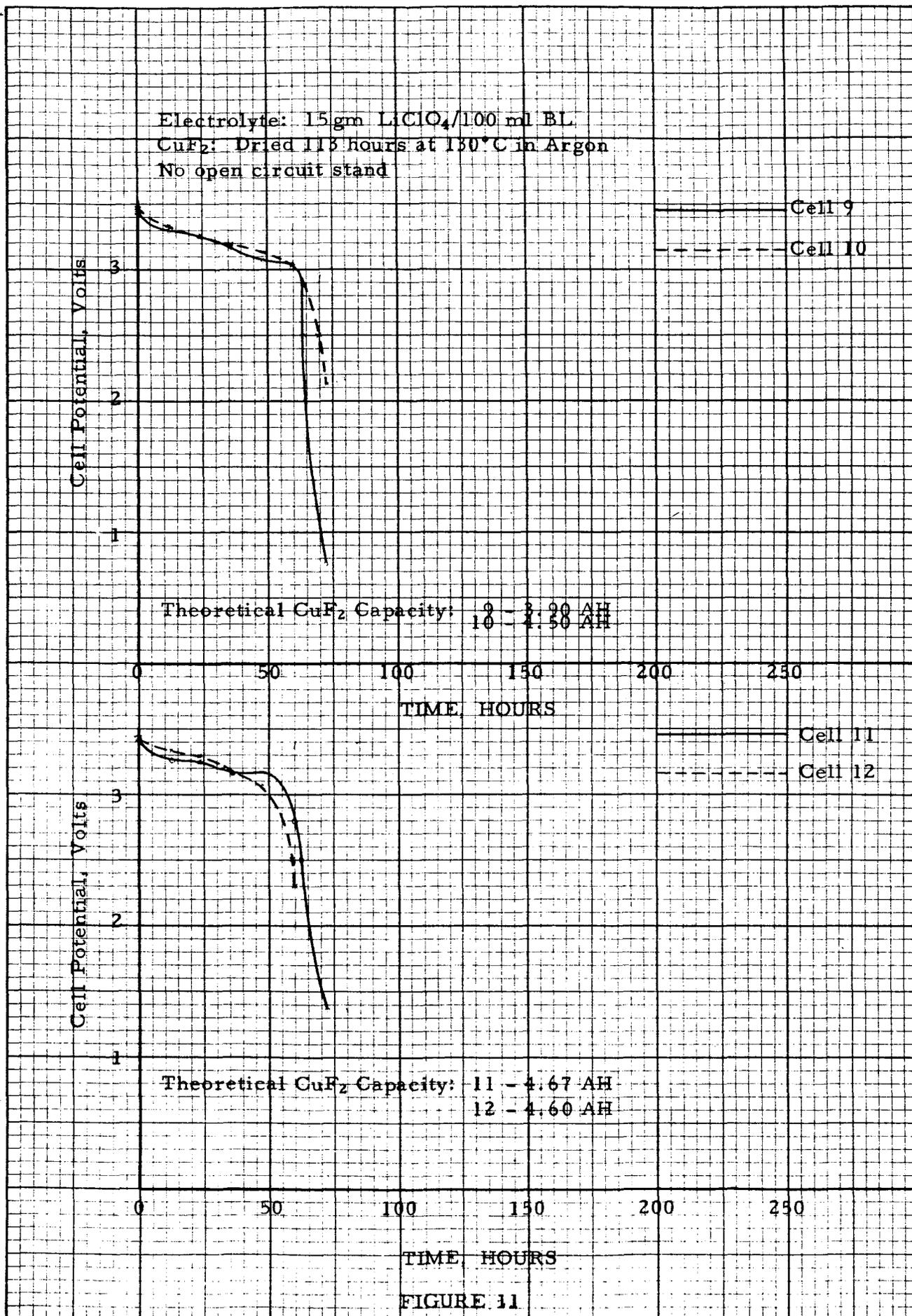
** CuF_2 : Dried in argon for 113 hours at 130°C

Electrolyte: 15 gm LiClO_4 /100ml BL.
 CuF_2 : Dried 16 hours at 130°C in Argon
 No open circuit stand



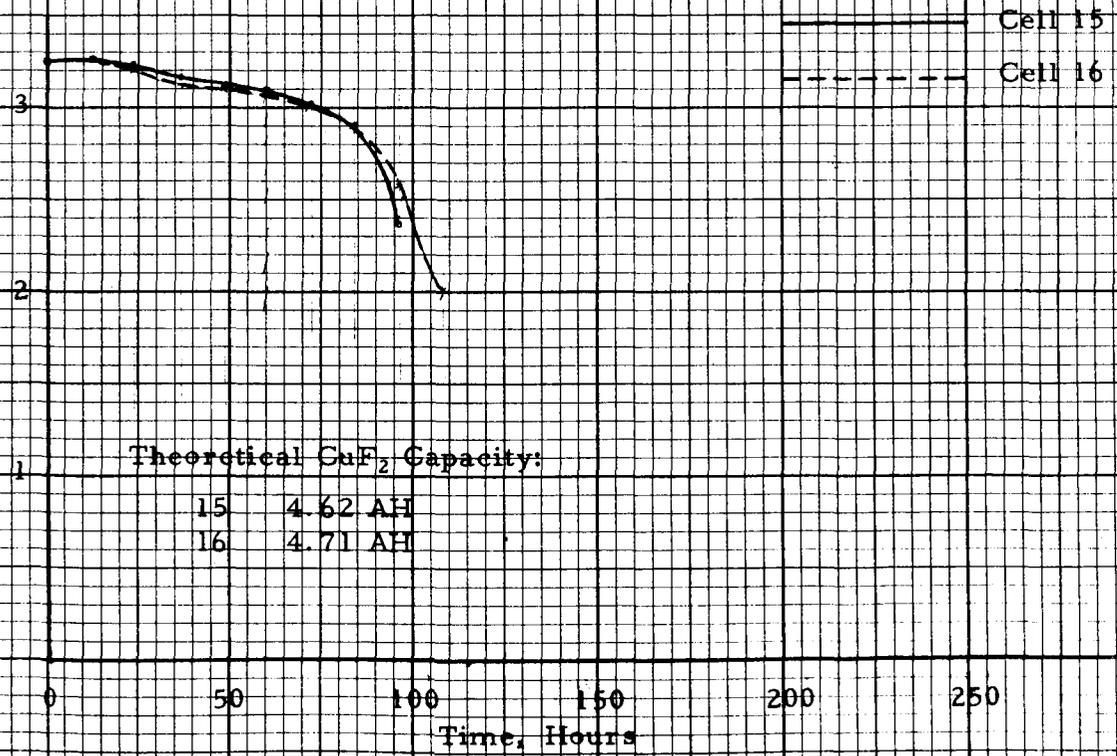
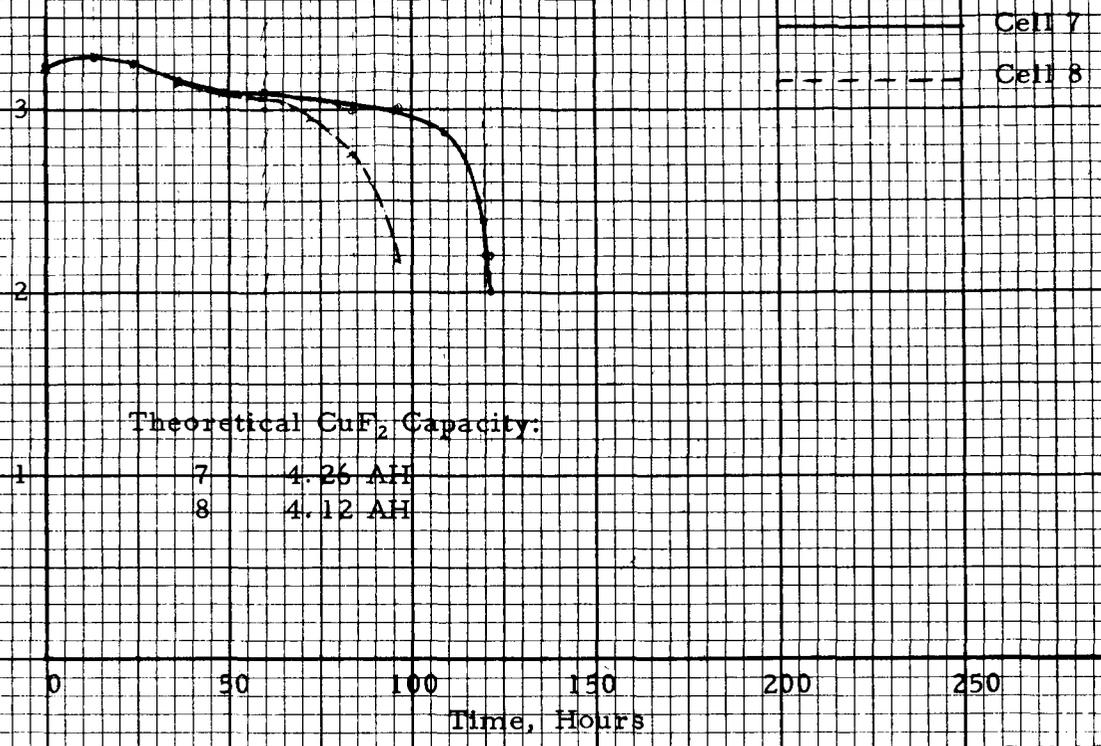
PERFORMANCE OF CuF_2 -Li CELLS

FIGURE 10

PERFORMANCE OF CuF_2 -Li CELLS

LTA #640-10

Stand Conditions: 2 weeks; -15°C
Discharge Conditions: 200 Ω; +35°C



PERFORMANCE OF CuF_2 -Li CELLS
FIGURE 12

4. APPENDIX

4.1 X-RAY ANALYSIS OF CuF_2

A. Preparation of Sample

About 10 g of the material to be analyzed is delivered under argon into a "Hi-speed" micronizer blender and ground for ca. 20 seconds. The material is then transferred to a polyethylene envelope, and the latter is heat sealed.

Prior to mounting on the diffractometer, the powder is pressed by hand into a 1/16 inch thick aluminum die which has been taped to a microscope slide. A second slide is then taped to the opposite side of the die, and the original slide is removed leaving a smooth plane of compacted material.

B. Analysis

A Phillips Model 12045B/3 X-ray generator is used in conjunction with Phillips No. 12096 Control Panel and No. 52090 Minneapolis-Honeywell Strip Chart Recorder. The sample is rotated from 80° to 10° Bragg angle at the rate of 1 degree/minute under monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$).

C. Calculation

1. $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$

The highest amplitude on chart between the limits of 18.4 and 18.6 degrees is selected, and percent $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ is calculated

$$\% \text{CuF}_2 \cdot 2\text{H}_2\text{O} = .0227 \times \text{amplitude} \times \text{scale factor.}$$

2. CuO

The highest amplitude between the limits of 38.6 and 38.8 degrees is selected, and percent CuO is calculated

$$\% \text{CuO} = .0417 \times \text{amplitude} \times \text{scale factor.}$$

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